

MÖSSBAUER SPECTROSCOPY OF IRON IN COAL

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INTRODUCTION

Metallic elements (Na, Mg, Al, Si, K, Ca, Ti, Fe) which occur abundantly in the ash obtained from the combustion of coals are present in the original coals partly as inorganic constituents or minerals. The identification of minerals present usually does not account quantitatively for several of these elements, and it is supposed that some sort of organic bonding with the coal is involved. The nature of this bonding in most coals has not been determined. Changes in the infra-red spectra of lignites and brown coals following acid and alkali treatment indicate the presence of metallic salts of carboxylic acids (1,2,3). For higher rank coals, little or nothing is known about the structures of the metallic elements "organically bound". In the case of iron, for example, it has not been determined whether the so-called "organic" iron is in the ferrous or ferric state, to what element or elements the iron is bonded, or whether there is more than one form of "organic" iron. The term "organic" must be interpreted with care; the nature of the bonding is uncertain; and presumably could be ionic, coordinate, or organo-metallic.

Mineral components containing iron can often be identified petrographically. Pyrite (FeS_2) is common, both as distinct nodules and as veins, often intertwined with carbonaceous macerals. An electron microprobe study of several coals (4) revealed, however, many examples which lacked a correlation between Fe and S distributions. In some cases Fe was distinctly associated with Si and Al, suggesting incorporation in an aluminosilicate gel or kaolinite. A strong parallelism of Fe and Ca (but not Si, Al, K, or S) in one specimen suggested the presence of Fe as carbonate or possibly oxide. In some cases the Fe showed fairly uniform distribution with no apparent correlation with other ash-forming elements. This presumably could be "organic" iron.

Mössbauer spectroscopy has been employed to study the chemical properties of iron in a great variety of natural materials: oxides and oxyhydroxides (5,6), sulfides (7,8), numerous silicate minerals (5,6,9,10,11,12), ilmenite and related titanium minerals (5,13), siderite (6), jarosites (5,14), löllingite (15), ordinary chondrite meteorites (16), carbonaceous chondrites (17), an achondrite (16), and several tektites (11).

Recent general articles on Mössbauer spectroscopy (18,19,20,21,22) discuss the interpretation of spectra in terms of the chemical state of iron, including its oxidation state, bonding, and environmental symmetry. The isomer shift (δ), quadrupole splitting (Δ), line width (Γ), line intensities, and a comparison of the spectra obtained at room temperature and at liquid- N_2 temperature are useful.

We have undertaken Mössbauer studies to characterize non-mineral iron in

coal. A major advantage of the Mössbauer technique is that the iron is observed without altering its chemical state or environment. The relatively low atomic number of the major elements present makes it possible for small amounts of iron to be observed in rather large amounts of coal. Samples of whole coal and vitrain as free as possible from minerals were selected in order to minimize mineral-iron interference, and a few samples whose chemical analysis indicated "organic" iron were included.

EXPERIMENTAL PROCEDURES

Nine specimens, vitrain or whole-coal, of seven coals with rank from lignite (72% C) to anthracite (95% C) were used. Their designations and geographic origins are given in Table 1, in order of increasing carbon content.

Table 2 is a compilation of the analytical data for C, H, N, S, Fe, ash, and O (by difference) on samples of these materials, as determined by the Coal Analysis group at the Bureau of Mines. The total iron in the coal was determined by ash analysis. HCl-soluble iron was determined by treating a separate powdered sample with 25% HCl to extract any iron present as carbonates, oxides, sulfates, etc. Pyrite iron was then removed by treating the HCl-leached coal with 25% HNO₃ to dissolve the iron combined with sulfur; the extract was evaporated to dryness to expel oxides of nitrogen, and the residue was dissolved in HCl. In each case the iron was reduced with SnCl₂, the slight excess of which was eliminated with HgCl₂. The reduced iron was titrated with potassium dichromate. "Organic" iron was then calculated by subtracting the two acid-soluble iron contents from the total iron. The resulting iron contents are listed in Table 2 as: total, HCl-soluble, pyrite, and "organic".

Mössbauer spectra were obtained on coal samples that were ground in a mortar and pestle. A cylindrical cell, open on one end with a circular aperture of 7.14 cm², was made by gluing a sheet of lucite 1/32" thick with Duco cement to the bottom of a circular wall made from a paper card. A 3.50-g sample was then placed into this cell. The top window, also 1/32" lucite, was then cemented in place. The sample mass per unit area was thus held constant at 0.490 g cm⁻². Inorganic iron compounds and mineral samples were ground and mounted either between two lucite sheets held together with Duco cement, or by mixing the solid with acetone and Duco cement and allowing this mixture to harden on a lucite sheet. This latter method was used only when the sample would not interact with acetone or the cement. The area for these samples was also 7.14 cm². All of the materials used in this investigation contained natural iron with presumably 2.19 atom % Fe⁵⁷.

The Mössbauer spectrometer incorporates a Nuclear Science and Engineering Corporation Model-B lathe-type drive modified in this laboratory for automatic operation. The operating mode employs constant velocity, advanced in increments of 0.05 mm s⁻¹. The detector of the 14.4-keV Co⁵⁷ → Fe⁵⁷ gamma radiation is a Reuter-Stokes proportional tube containing 10% methane in krypton, feeding through a single-channel analyzer set at 11 - 17 keV. Absorbers were mounted on the moveable table perpendicular to the radiation beam. The stationary source consists of ~ 5 mCi of Co⁵⁷ diffused into chromium metal. A Baird-Atomic scanning count integrator and Varian chart recorder plot the number of counts in a constant time interval at each velocity in succession.

Powdered samples of sodium nitroprusside gave an isomer shift, relative to the Co⁵⁷-Cr source, of -0.11 mm s⁻¹, and a quadrupole splitting of 1.68 mm s⁻¹. With this source a line width of 0.25 mm s⁻¹ was observed with an absorber containing 5 mg cm⁻² of Fe as K₄Fe(CN)₆·3H₂O. The estimated uncertainty in the velocity setting is about 2% of the velocity and the estimated uncertainty in derived spectral parameters is ~ 0.05 mm s⁻¹. The counting time at each velocity was ~ 5

Table 1. Designations, geographic origins, and adjusted* carbon contents of coal samples used.

Code #	Designation†	Geographic Origin	Mass fraction C* (%)
A	Indian Head lignite	Zap Bed, Indian Head Mine, N. Dakota	72.2
B	Harmatten vitrain, hvcb	No. 7 Bed, Harmatten Mine, Illinois	76.5
C	Corbin coal, hvab	High Splint Bed, Lynch Mine, Corbin Plant, Ky.	84.3
D	Bruceton vitrain, hvab	Pittsburgh Bed, Bruceton Mine, Pa.	84.2
E	Bruceton coal, hvab	Pittsburgh Bed, Bruceton Mine, Pa.	84.7
F	Jewell Valley coal, mvb	Jewell Bed, Jewell Valley Coal Co., Va.	90.3
G	Pocahontas No. 4 vitrain, lvb	Pocahontas No. 4 Bed, McAlpine No. 2 Mine, W.Va.	90.3
H	Pocahontas No. 4 coal, lvb	Pocahontas No. 4 Bed, McAlpine No. 2 Mine, W.Va.	90.4
I	Dorrance anthracite vitrain	Dorrance Mine, Lehigh Valley Coal Co., Pa.	92.7

* Adjusted to moisture- and ash-free basis. Calculated from C and ash contents of Table 2.

† h = high; m = medium; l = low; v = volatile; b = bituminous; a, c = sub-classifications of high-volatile coals.

Table 2. Analytical data on coal samples used.

Sample No.	Mass Fraction Fe (%) [*]			Mass fraction (moisture-free basis) (%) [†]						
	Total	HCl-sol.	Pyrite	"Organic" [†]	Ash	C	H	N	S	O [†]
A (a)	0.13	-	-	-	5.6	68.2	4.6	0.6	0.6	20.2
B (a)	0.81	0.40	0.27	0.14	1.0	75.8	5.3	1.3	1.8	14.8
C (a)	0.23	0.06 [§]		0.17	3.8	81.1	5.3	1.6	0.5	7.7
D (a)	0.62	-	0.33	(0.29) [#]	1.4	83.0	5.4	1.6	0.8	7.8
(b)	0.33	0.02	0.21	0.11						
E (a)	4.18	-	3.85	(0.33) [#]	1.9	83.1	5.6	1.6	0.7	7.1
(b)	0.32	0.06	0.20	0.06						
F (a)	1.39	0.24 [§]		1.16	1.8	88.7	4.6	1.4	0.5	3.0
(b)	0.47	0.37	0.08	0.02						
G (a)	0.46	0.03	0.00	0.44	1.2	89.2	4.6	1.5	0.8	2.7
H (a)	0.43	0.15	0.00	0.28	2.6	88.1	4.3	1.3	0.6	3.1
(b)	0.39	0.21	0.04	0.14						
I (a)	0.41	0.00	0.03	0.38	1.8	91.0	2.5	1.0	0.8	2.9
(b)	0.57	0.11	0.20	0.26						

† By difference.

* In sample as received, before drying.

§ Includes both HCl-soluble and pyrite iron.

Includes both "organic" and HCl-soluble iron.

† Determined on samples other than those used for Mössbauer and iron determinations.

minutes, yielding ~ 600,000 counts and a relative standard deviation < 0.15%. The velocity region scanned for each sample was from -2.00 mm s^{-1} to about $+4.00 \text{ mm s}^{-1}$.

Most measurements were made at room temperature. A cryostat made from styrofoam was mounted on the moveable table of the instrument for low-temperature measurements. The sample was placed in this and submerged in liquid N_2 . The spectrum of each coal sample was run twice at room temperature, before and after the spectrum was taken at liquid- N_2 temperature.

Spectral parameters were generally read from plotted spectra. The data from sample F(a) were fitted to a double Lorentz curve by a least-squares program using an IBM 7040 computer. Isomer shifts are reported (in mm s^{-1}) with respect to the isomer shift of sodium nitroprusside. Quadrupole splittings are reported (in mm s^{-1}) as the velocity differences between the minima of two associated absorption lines.

DATA

Room-temperature spectra for the nine coal samples are illustrated in Figure 1. Each spectrum shows neither, either, or both of just two components: (1) a close doublet similar to those of pyrite and marcasite, and (2) a wide doublet similar to those of many ferrous compounds. Table 3 lists the Mössbauer parameters, including the fractional peak absorptions, for what we will call respectively the pyrite and non-pyrite resonances. Isomer shifts and quadrupole splittings obtained with our instrument on some powdered iron compounds and minerals which were regarded as possibilities for the non-pyrite spectrum appear in Table 4.

The parameters observed for the pyrite iron are: isomer shift (δ) = $+0.54 \text{ mm s}^{-1}$; quadrupole splitting (Δ) = 0.58 mm s^{-1} . All of the coals having a non-pyrite absorption as shown in Figure 1 have: $\delta = +1.38 \text{ mm s}^{-1}$; $\Delta = 2.62 \text{ mm s}^{-1}$. The computer analysis of sample F(a) indicated both lines in the spectrum had widths (Γ) of 0.39 mm s^{-1} ; their intensity ratio is within 5% of unity.

Liquid- N_2 spectra showed the same absorption peaks as at room temperature, with $\delta = +0.65 \text{ mm s}^{-1}$ and $\Delta = 0.58 \text{ mm s}^{-1}$ for pyrite and $\delta = +1.47 \text{ mm s}^{-1}$ and $\Delta = 2.78 \text{ mm s}^{-1}$ for the non-pyrite iron.

INTERPRETATION

The isomer shift is a function of nuclear properties and the electron density at the absorbing nucleus relative to that of the source or a standard absorber, such as sodium nitroprusside (23,24). As the electron density at the iron nucleus, due essentially only to s electrons, increases, the isomer shift decreases algebraically. Thus, ferrous compounds have a more positive isomer shift than ferric compounds, as the additional 3d electron of the former increases the shielding effect on the 3s electrons and thereby decreases their density at the nucleus (18). For ferric iron, isomer shifts (relative to sodium nitroprusside) have been observed in the range -0.1 to $+1.1 \text{ mm s}^{-1}$, and for ferrous iron from -0.1 to $+1.6 \text{ mm s}^{-1}$.

Quadrupole splitting into a two-line spectrum occurs when the iron nucleus is in an asymmetric electric field. The field consists of two parts, (1) that produced by the electrons of the iron atom, including those shared with adjacent atoms, and (2) that resulting from charges of the surrounding atoms; each part can contribute to asymmetry at the nucleus. Ferric compounds show quadrupole splittings from zero to about 2.3 mm s^{-1} ; here the asymmetry is caused chiefly by charges of the surrounding atoms. Ferrous compounds show larger values, from zero to $\sim 3.3 \text{ mm s}^{-1}$. Ferrous iron can exist in either a high-spin or a low-spin

Table 3. Room-temperature Mössbauer spectral parameters for coal samples*

Sample No.	Pyrite iron			Non-Pyrite iron		
	Isomer shift† (mm s ⁻¹)	Quadrupole splitting (mm s ⁻¹)	Fractional absorption (%)	Isomer shift† (mm s ⁻¹)	Quadrupole splitting (mm s ⁻¹)	Fractional absorption (%)
A (a)	-	-	N.O.‡	-	-	N.O.‡
B (a)	0.50	0.55	1.6	-	-	N.O.
C (a)	-	-	N.O.	1.39	2.65	2.3
(b)	-	-	N.O.	1.30	2.65	2.1
D (a)	0.51	0.55	3.6	-	-	N.O.
(b)	0.53	0.48	3.6	-	-	N.O.
E (a)	0.50	0.58	22.7	1.41	2.70	2.6
(b)	0.50	0.53	2.3	-	-	N.O.
(c)	0.50	0.53	1.7	-	-	N.O.
F (a)	-	-	N.O.	1.38	2.62	11.0
(b)	-	-	N.O.	1.39	2.65	5.5
G (a)	-	-	N.O.	1.38	2.65	1.5
(b)	-	-	N.O.	1.38	2.65	1.0
H (a)	0.54	0.60	1.3	1.39	2.65	1.5
(b)	0.59	0.60	1.7	1.36	2.60	1.7
I (a)	-	-	N.O.	-	-	N.O.
(b)	0.56	0.65	1.0	-	-	N.O.

* Weighing 3.50 g and distributed evenly over 7.14 cm².

‡ May include marcasite.

† With respect to center of sodium nitroprusside spectrum.

‡ Zero-point uncertain by 0.10 mm s⁻¹.

‡ N.O. = not observed; in general, < 0.5%.

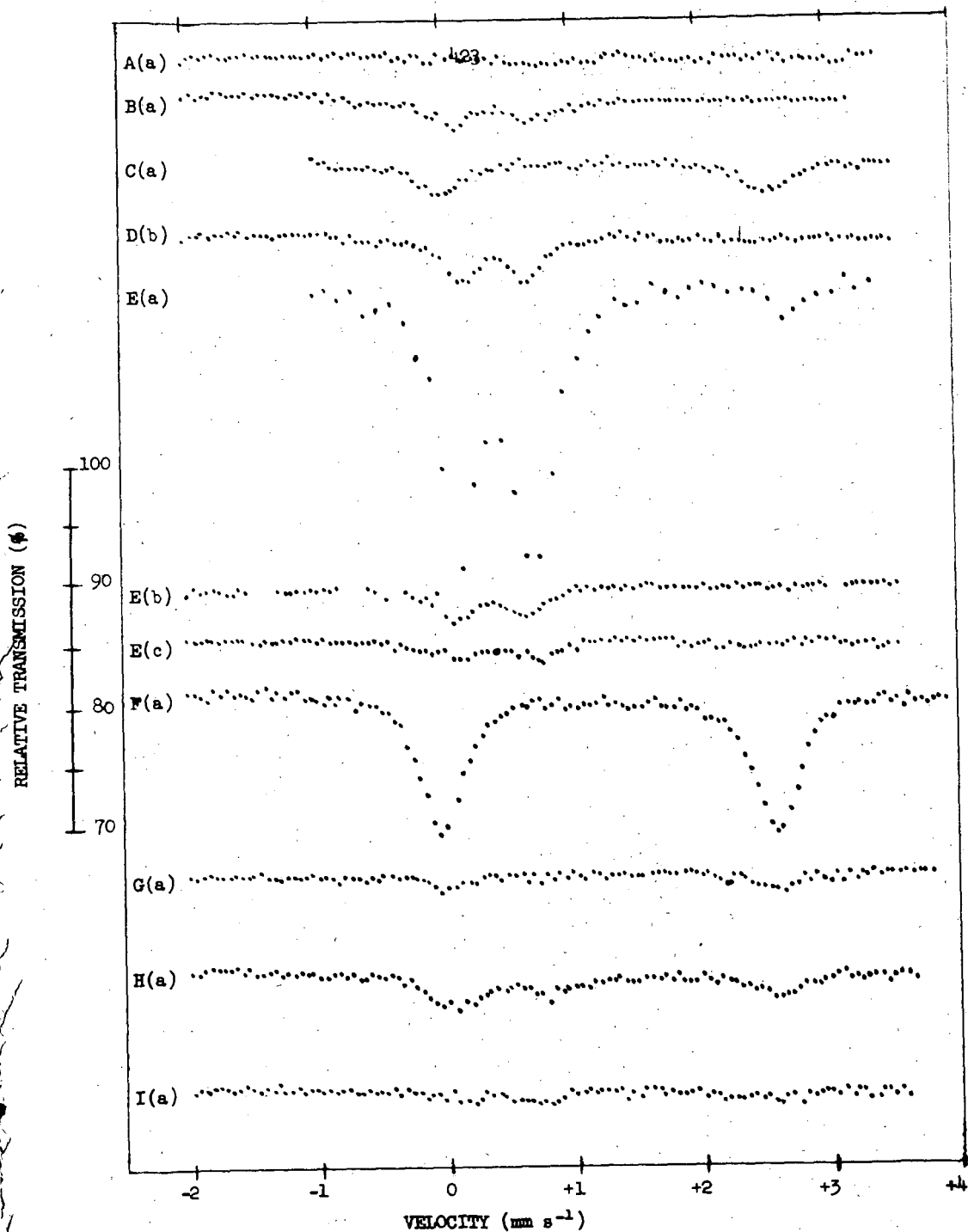


Figure 1. Mössbauer spectra of coal samples. In most cases, each point represents $\sim 600,000$ counts. The source was Co^{57} diffused into chromium metal. To convert the velocity scale to the sodium nitroprusside scale, add 0.11 mm s^{-1} to the indicated values.

state, depending on the strength of the ligand field around the central iron atom. In the high-spin configuration the large asymmetry of the valence shell results in considerable asymmetry at the nucleus; low-spin ferrous compounds have smaller field asymmetries, which are due chiefly to the external environments only.

Pyrite and marcasite, respectively stable and metastable forms of FeS_2 , are low-spin ferrous compounds. Isomer shifts and quadrupole splittings observed in this laboratory (Table 4) are in agreement with those of Temperley and Lefevre (8). The parameters of the two minerals are so similar that the spectra cannot be resolved when both are present. A comparison of the data in Tables 3 and 4 confirms the conclusions from petrographic (25) and x-ray diffraction (26) studies that the iron sulfide in coal consists mainly of pyrite.

From the Mössbauer data on the non-pyrite iron observed in several coal samples (Figure 1 and Table 3), it can safely be concluded that this iron is in a high-spin ferrous state. Furthermore, the combination of such high values of both isomer shift and quadrupole splitting has been reported only in octahedrally-coordinated high-spin ferrous compounds, so it is highly probable that the non-pyrite iron in coals is in octahedral coordination. Neither the analytical nor the Mössbauer data yields a distinction between inorganic or organic minerals or compounds.

The natural line width (Γ_0) of the Fe^{57} gamma radiation corresponds to a velocity difference of 0.0973 mm s^{-1} (27), and the minimum observable line width (Γ) in a Mössbauer spectrum is twice this, 0.195 mm s^{-1} . Inhomogeneities in the source and absorber, instrumental "noise", unresolved quadrupole splitting, and atomic spin-spin relaxation effects (22,28,29) increase the apparent line widths, and further widening occurs with thick absorbers (30). The minimum width we have observed with our instrument is 0.25 mm s^{-1} for a very thin absorber. The value of $\Gamma = 0.39 \text{ mm s}^{-1}$ observed for the strongest non-pyrite iron spectrum (sample F(a)) indicates that this doublet is caused by a fairly well-defined iron compound or mineral, though some inhomogeneity may be present.

A large number of iron compounds have strong Mössbauer absorptions (large recoil-free fractions) at room temperature. Some ferrous compounds show little or no absorption at room temperature, but at liquid- N_2 temperature the intensity is strongly enhanced (31,32). We have observed this effect with ferrous stearate, which must be cooled to liquid- N_2 temperature before resonant absorption is detected. Herzenberg and Toms (5) have observed that samples of $\gamma\text{-Fe}_2\text{O}_3$ and $\delta\text{-FeOOH}$ give nonresonant absorption at room temperature. These would probably exhibit an effect at liquid- N_2 temperature. Lack of such an effect in the coals is interpreted to mean that there are no compounds present in significant amounts that do not have appreciable resonant absorption at room temperature.

Isomer shifts and quadrupole splittings depend on the temperature. A second-order Doppler effect (22) decreases the isomer shift as the temperature is increased. Quadrupole splittings for high-spin ferrous compounds are affected by temperature much more strongly than those of other iron compounds because the population of the d_z levels of iron in an octahedral field is determined by a Boltzmann distribution (18,22). For example, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ shows a change of δ from $+1.53$ to $+1.56 \text{ mm s}^{-1}$ and of Δ from 3.19 to 3.47 mm s^{-1} in going from room to liquid-nitrogen temperature (18). The observed change in the non-pyrite iron spectrum in coal of δ from $+1.38$ to $+1.47 \text{ mm s}^{-1}$ and of Δ from 2.62 to 2.78 mm s^{-1} is in agreement with our assignment to this class of compounds.

In some iron compounds where the Mössbauer absorption ordinarily shows a 6-line hyperfine structure as a result of a magnetic field at the nucleus, very

finely comminuted samples show instead a two-line pattern at room temperature as a result of thermal disruption of the macroscopic magnetic domains. Kündig et al. (33) observed this effect in $\alpha\text{-Fe}_2\text{O}_3$ in particles of $\sim 50\text{-}\text{\AA}$ diameter, but at liquid- N_2 temperature the 6-line pattern was observed. The absence of any magnetic splitting in the coal spectra at room- or liquid- N_2 temperatures probably rules out the possibility that the non-pyrite doublet is caused by a magnetically ordered material (such as Fe_2O_3 , Fe_3O_4 , FeC_3 , FeS , or metal) present as very small particles.

Inequality in the intensity of the components of a doublet may result from the anisotropy of the absorption cross section relative to the crystal axes when (1) a single-crystal absorber is oriented preferentially with respect to the optical axis, or (2) there is anisotropy in the recoilless fraction of the split $3/2$ state; the latter condition results in unequal absorption even with powdered samples (Goldanskii effect) (20,21). Most of the samples used in this work were powdered, so only the second effect could be operative, except for biotite, which was mounted as a sheet. The essential equality of intensity of the two non-pyrite coal spectrum lines would eliminate any compounds showing unequal absorption in powdered samples as possible causes of this absorption.

At the present state of Mössbauer spectroscopy, the identification of an unknown compound from its spectrum can only be made by finding a known compound having the same spectrum and temperature dependence. We have been unable to find any published combination of spectral parameters, for either natural or synthetic iron compounds, which match that of the non-pyrite iron in coal. Ankerite (Table 4), which has not been reported previously, likewise does not match.

In Figures 2 and 3 we have plotted Δ versus δ for all single- or two-line iron spectra for which we have been able to obtain data (5,6,8,9,10,11,14,18,31,34,35,36,37,38,39,40). Attention is called to the variations in δ and Δ within isomorphous silicate series (olivines, pyroxenes) in which the Fe/Mg ratio varies. Many silicate minerals show two or more coupled Mössbauer doublets, eliminating from consideration many points near the coal point on the plots. Biotite gives an apparent 2-line spectrum with δ and Δ similar to the coal spectrum, but with decidedly unequal intensities (our measurement), which persist in powdered samples (6), and which can be resolved into a coupled doublet (9), whereas the coal spectrum is symmetrical. Even considering the compositional variations and the uncertainties of measurement, it is apparent that the non-pyrite iron in coal is distinct from any compound whose Mössbauer spectrum is known. Minerals excluded include oxides and oxyhydroxides, sulfides and related compounds, the carbonates siderite and ankerite, titanian minerals, and the many silicates examined.

Some ferrous complexes of pyridines (35) and 1,10-phenanthrolines (37) have similar though non-matching δ and Δ values. These comparisons suggest that the non-pyrite iron could be bound to heterocyclic nitrogen aromatic groups in the coal macerals, or possibly in a clay-like silicate mineral or gel.

An attempt was made to correlate the Mössbauer absorption intensities in the coals with the analytical data. Mössbauer spectra were determined on mixtures of pyrite in carbon, and the fractional peak absorption was plotted against the mass fraction of pyrite iron. In a few coal samples the Mössbauer absorption and the analytically determined amount of iron as "pyrite" did agree with the above plot, but in others the agreement was poor. This may be due to the inadequacy of the chemical method for determining pyrite iron, and to differing matrix effects in the coals and the standards. Likewise, a poor correlation was found between the non-pyrite iron absorption in coals and the amount of "organic" iron deduced from the chemical analyses, although the sample with the highest "organic" iron, Jewell Valley coal F(a), showed the strongest non-pyrite Mössbauer spectrum.

Table 4. Room-temperature isomer shifts and quadrupole splittings for polycrystalline iron compounds and minerals

Compound or Mineral	This Work		Other Work		Ref.
	$\delta^*\S$	$\Delta\S$	$\delta^*\S$	$\Delta\S$	
Pyrite, FeS_2	0.54	0.60	0.55	0.61	8
Marcasite, FeS_2	0.51	0.50	0.52	0.51	8
Siderite, $(\text{Fe},\text{Mg})\text{CO}_3$	1.47	1.78	1.47	1.80	6
Ankerite, $(\text{Ca},\text{Mg},\text{Fe})\text{CO}_3$	1.46	1.50	-	-	-
Olivine, $(\text{Mg},\text{Fe})_2\text{SiO}_4$	1.39	2.95	1.39	3.04	10
Biotite, $\text{K}(\text{Mg},\text{Fe})_3(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$	1.36	2.50	1.27 1.46	2.41 2.81	9
Tourmaline, $\text{Na}(\text{Mg},\text{Fe})_3\text{Al}_6(\text{BO}_3)_3(\text{Si}_6\text{O}_{18})(\text{OH})_4$	1.30	2.38	Fe^{+2} 1.19 Fe^{+2} 1.44 Fe^{+3} 0.99	2.10 2.61 0.91	10
Ferrous sulfate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	1.56	3.05	1.53	3.19	18
Ferrous acetate, $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_2$	1.45	2.23	-	-	-
Ferrous stearate, $\text{Fe}(\text{C}_{18}\text{H}_{35}\text{O}_2)_2$	0.66†	0.70†	-	-	-
Non-pyrite iron in coal	1.38	2.62	-	-	-

* Respect to center of sodium nitroprusside spectrum.

† At liquid nitrogen temperature; no resonant absorption observed at room temperature.

§ In mm s^{-1} .

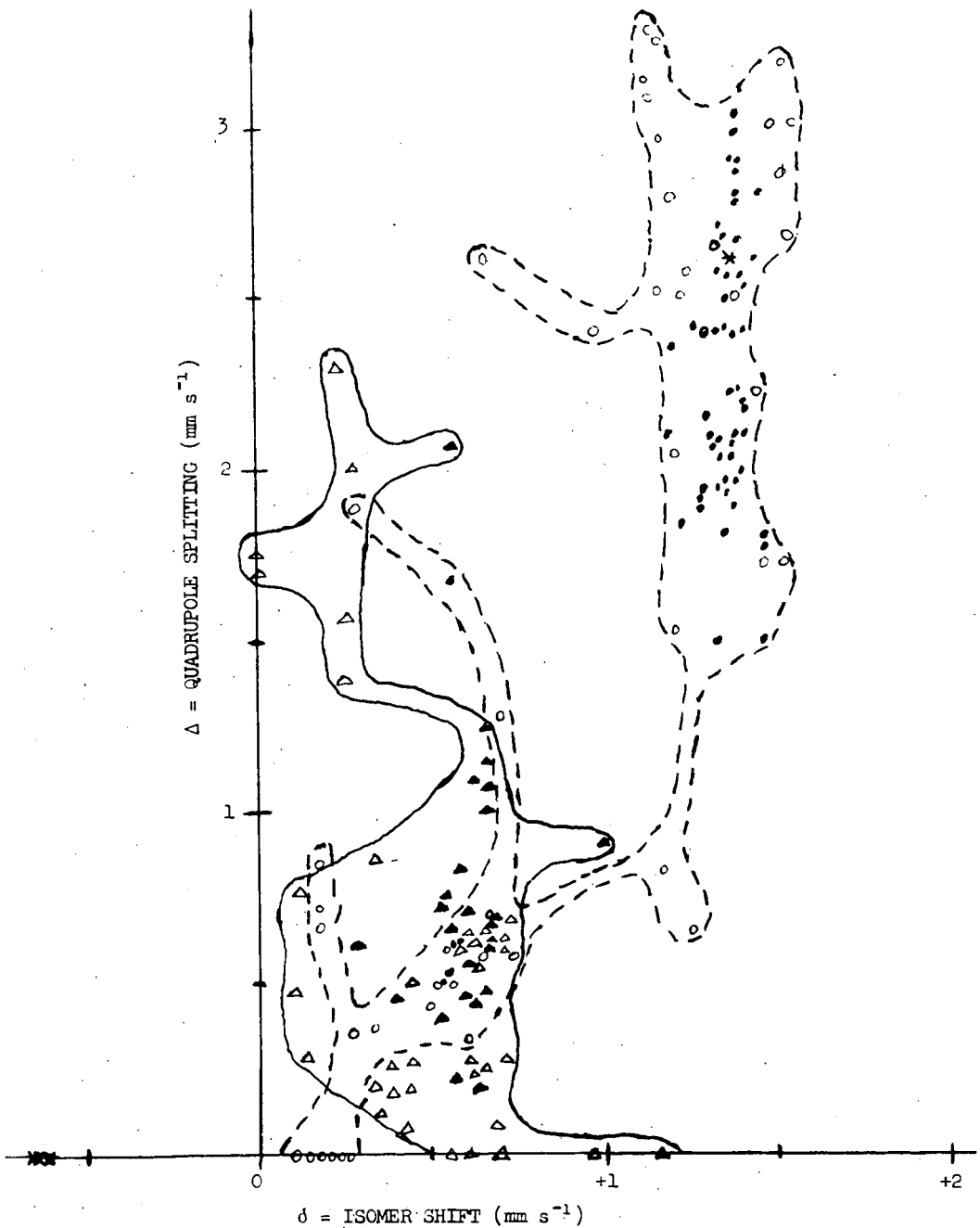


Figure 2. Representative plot of quadrupole splitting versus isomer shift (relative to sodium nitroprusside) for: — ferric compounds (Δ) and minerals (\blacktriangle); ---- ferrous compounds (\circ) and minerals (\bullet); ferrate compounds (\times), and the non-pyrite iron found in coal (*).

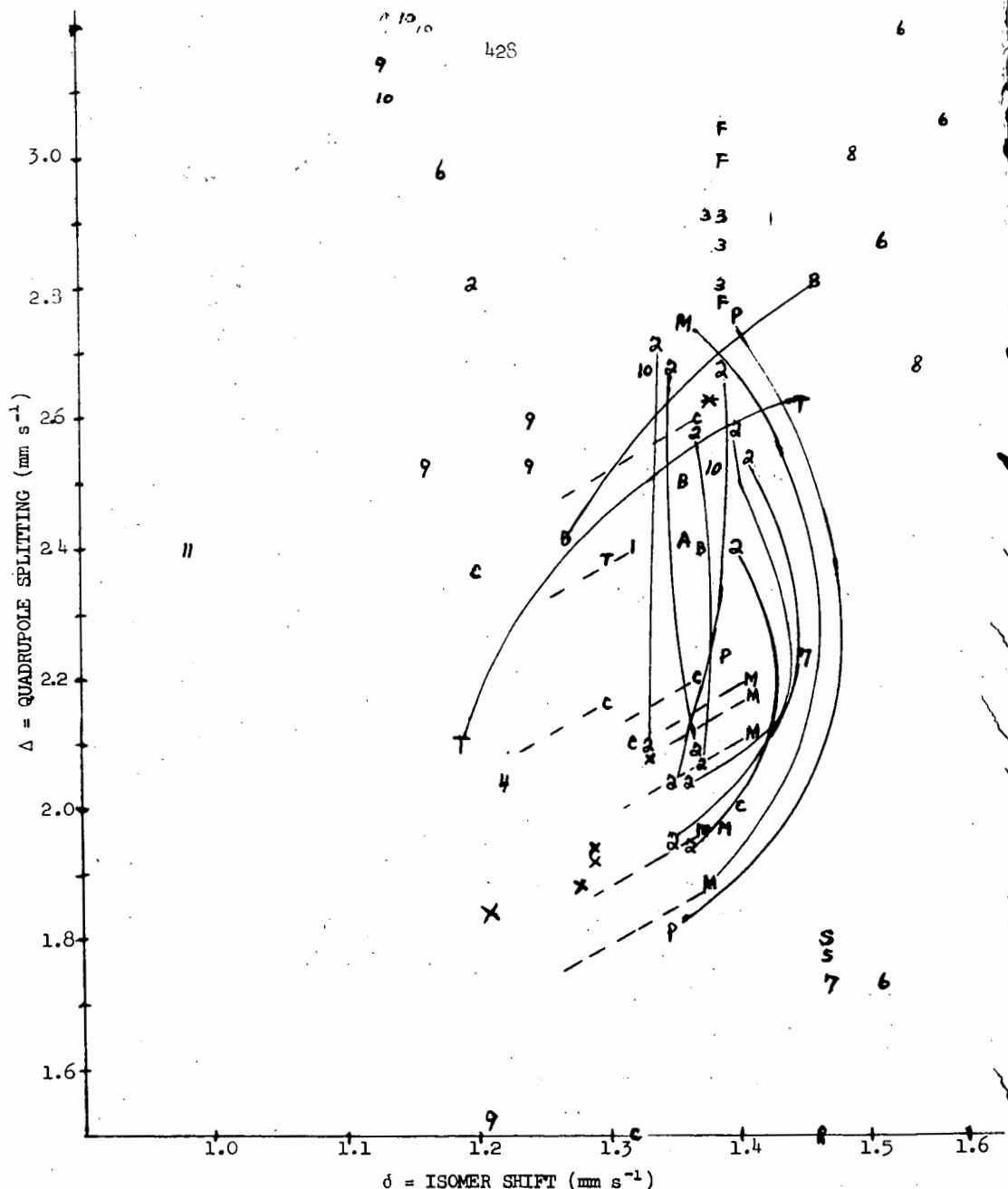


Figure 3. Enlarged section of Figure 2, showing quadrupole splitting versus isomer shift relative to sodium nitroprusside for two-line ferrous spectra. Lines connect pairs of points which are observed together in the same mineral or compound. Dashed lines indicate that a ferric spectrum is associated with the plotted ferrous point. Synthetic compounds: 1-ferrianite (synthetic mica), 2-synthetic pyroxenes, 3-synthetic olivines, 4-welding glass 5-germanium spinel, 6-oxy-salts, 7-carboxylates, 8-halides, 9-pyridine complexes, 10-phenanthroline complexes, 11-ferrous hemoglobin. Natural materials: A-actinolite, B-biotite, C-clay minerals, F-fayalite and olivine, M-clinopyroxenes, P-orthopyroxenes, R-ankerite, S-siderite, T-tourmaline, X-tektites, *-non-pyrite iron in coal.

CONCLUSION

In summary, several coal samples contain a form of iron which exhibits a hitherto unobserved Mössbauer spectrum, in addition to the well-known pyrite spectrum. The non-pyrite iron is ferrous, in a high-spin configuration, in octahedral symmetry, and apparently in a rather well-defined state. Comparisons with known compounds suggest that this iron may be bound in the coal macerals to heterocyclic nitrogen aromatic groups, though a clay-like silicate mineral or gel is a possibility. Mössbauer spectrometry can at the very least indicate the most suitable coal samples for further studies of this iron by chemical and other methods. It should ultimately permit unambiguous identification of the iron in coal with synthetic compounds or analogs. We intend to pursue this line of investigation.

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